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Crystal and Molecular Structures of Bis-tetramethylammonium Hexabromouranate (IV) and Bis-tetramethylammonium Dioxotetrabromouranate (VI)

Donald Dean Dickerson

CRYSTAL AND MOLECULAR STRUCTURE OF

bis-TETRAMETHYLAMMONIUM HEXABROMOURANATE (IV)

AND

bis-TETRAMETHYLAMMONIUM DIOXOTETRABROMOURANATE (VI)

BY

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This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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INTRODUCTION

The purpose of this work was to study bond lengths in uranium halide complexes by means of x-ray crystallography. In order to prepare the uranium complexes, a synthesis had to be found that would allow uranyl acetate to be used as the starting material.

Two complexes, bis-tetramethylammonium hexachlorouranate (IV) and bis-tetramethylammonium dioxotetrachlorouranate (VI), were chosen for crystal studies. U--Br bond lengths were determined for each complex. Carbon and nitrogen were located for the U(IV) complex. A full matrix least squares refinement and electron density maps were used to find atom and temperature parameters.

HISTORICAL

Before World War II, progress made in the field of uranium chemistry involved primarily work with uranium metal and an insignificant number of alloys and compounds. Most of the synthetic and spectroscopy work was done after 1946. Also, much of the work that has been done in both synthesis and structural determination has been classified, so that a literature search cannot contain all work that has been performed.

The following syntheses were used as references for finding a method suitable to this work. Although none of these syntheses could be used with uranyl acetate as the starting material, many of the individual techniques could be followed.

Previous Preparative Techniques

It has been reported by J. L. Ryan[1] that bis-tetraphenylarsonium hexachlorouranate (IV) can be made by allowing tetraphenylarsonium chloride, dissolved in ethanol, to react with a solution of uranium tetrachloride. This solution can be prepared by adding uranium tetrachloride to dilute HCl or by dissolving uranium metal in a 6N HCl solution.[2] By saturating nitromethane with bis-tetraphenylarsonium hexachlorouranate (IV), passing chlorine gas through this solution, and heating it in a sealed vial at 50--60°C, Ryan[1] was able to produce tetraphenylarsonium hexachlorouranate (V). This product proved to be extremely unstable in the presence of moisture.

Eberhard Stumpp reported preparing cesium hexachlorouranate (V) by adding uranium trioxide and cesium chloride to thionyl chloride and heating it for 24 hours at 180--200°C in a sealed tube.[3] Other alkali salts were also made in this manner.

Bis-triphenylphosphonium hexachlorouranate (IV) has been prepared by C. K. Jorgensen[4] by allowing triphenylphosphine, dissolved in acetone, to react with a U(IV) solution that had been prepared by dissolving uranium filings in 6N HCl. It was also reported that the bromine analogue could be prepared by using 6N HBr instead of HCl. Nitromethane was used as a recrystallizing solvent. This proves to be a fairly common solvent in uranium (IV) chemistry for it is polar enough to dissolve most U(IV) complexes. Also, as most U(IV) complexes oxidize easily to U(VI), the poor oxidizing ability of nitromethane makes it even more suitable.

A reduction synthesis can also be used to prepare bis-triphenylphosphonium hexachlorouranate (IV) as reported by Day and Venanzi.[5] Uranyl chloride was suspended in diethyl ether and granulated zinc amalgam was added. Dry HCl is passed through this mixture until the uranyl acetate dissolves to form a green U(IV) solution. This solution is then decanted into a solution of triphenylphosphine in diethyl ether. The product can then be separated and recrystallized from acetonitrile. The bromine salt can also be prepared by this method, using uranyl bromide and HBr.

Bis-tetramethylammonium hexachlorouranate (IV) and hexabromouranate (IV) may be prepared by the method described by Jorgensen,[4]

with the substitution of tetramethylammonium halide for triphenylphosphine. This method is also reported by Satten, Schreiber, and Wong.[6] In both reports, crystals of the bromine salt were grown by slow evaporation of the solution which formed when the ligand and U(IV) solutions were mixed. No mention was made of a recrystallizing solvent.

There have been two general methods reported for the preparation of uranyl halide complexes. Vicente[7] prepared complexes of the form $M_2UO_2Cl_4$ where M is a metal ligand. The metal chloride is added to a solution of UO_3 in concentrated HCl. The mixture is evaporated to dryness. The product is separated and recrystallized from water. Day and Venanzi[5] reported preparing both uranyl chloride and bromide complexes by adding the stoichiometric amount of ligand in solution in acetonitrile to the appropriate uranyl halide. The products were recrystallized from acetonitrile. Tetramethylammonium and triphenylphosphonium complexes have also been prepared in this manner.

Review of Spectral Properties

The visible absorption maximum for the uranyl ion is reported by Day and Venanzi[5] to appear between 400 and 450 nm and has fine structure. This is the only absorption maximum to appear in the visible region.

The U(IV) ion, however, has a series of peaks appearing between 458 and 850 nm. Satten, *et al.*,[6] have reported the absorption maxima of *bis*-tetramethylammonium $(TMA)_2$ and *bis*-triphenylphosphonium $(TPP)_2$

hexabromouranate (IV) salts, which are listed in the following table:

Compound	Absorption Maxima (nm)								
$(TMA)_2\ UBr_6$	851	797	678	667	652	620	---	---	---
$(TPP)_2\ UBr_6$	847	796	673	667	---	620	499	464	458

These spectra were taken as solid samples at 77°K, which explains the resolution of the fine structure. Jorgensen[4] reports the absorption maxima for the triphenylphosphonium complexes in solution at 594 and 634 nm for UCl_6^{--} and at 620, 650, and 670 nm for UBr_6^{--}.

Infrared spectra for the uranyl complexes have been reported by Satten and Young[8] and by Day and Venanzi.[5] The former reported that in $Cs_2UO_2Cl_4$ the uranyl asymmetric stretch occurs at 915 cm^{-1}. Day reports that this absorption band is found between 900 and 950 cm^{-1} for UO_2Cl_4 and UO_2Br_4.

Hoekstra[9] has found that the position of the uranyl band can yield a good approximation of the U--O bond distance. He notes that Badger's[10,11] relationship,

$$\underline{R}_{UO} = \beta \underline{F}_{UO}^{-1/3} + \underline{d}_{UO}$$

can be applied to this system. $\underline{R}_{UO}$ is the bond length, $\underline{F}_{UO}$ is the force constant in mdynes/Å, and β and $\underline{d}_{UO}$ are constants whose values are determined by the bonding elements. Hoekstra used a value of 1.08 for β and 1.17 for $\underline{d}_{UO}$. With these constants he was able to calculate U--O bond lengths that agree with the values found by x-ray structural analysis, to within experimental error.

The last bit of spectral data of interest here was also reported by Day and Venanzi.[5] They assigned an infrared absorption peak, appearing at 2430 cm^{-1} in the spectrum of bis-triphenylphosphonium hexachlorouranate (IV), to the P--H stretch. This absorption peak is used to substantiate the presence of the triphenylphosphonium ligand as opposed to either tetraphenylphosphonium or triphenylphosphine oxide ligands.

Structural Determinations of Uranium Complexes

The structure of tetraphenylarsonium hexachlorouranate (V) has been worked on by Jensen, Wilson, and Eiss.[12] It was found to be a monoclinic crystal and to have the space group symmetry of C_5^4-Cc. Lattice constants are; a = 23.22 Å, b = 6.8 Å, c = 18.22 Å, and the angle β = 93°. There are four molecules per unit cell which gives a calculated density of 1.925 g/cc. Experimental density is 1.974 g/cc. At this time only uranium, chlorine, and arsenic atoms have been located and the structure has been refined to a R factor of 0.20. The U--Cl bond distance was reported to be normal for this type of compound.

Staritzky and Singer[13] have reported x-ray data for two uranium complexes. Bis-tetramethylammonium hexachlorouranate was found to be face-centered cubic with a lattice constant of 13.03 Å and four molecules per unit cell. The analogous tetraethylammonium salt is orthorhombic in space group D_{2h}^{23}-Fmmm and has lattice constants of; a = 14.2 Å, b = 14.7 Å, c = 13.3 Å. There are four molecules per

unit cell.

X-ray data was also included for two uranyl complexes analogous to the compounds above. The tetramethylammonium salt is tetragonal with the space group C_{4h}^5-I4/m with a = 9.12 Å and b = 11.77 Å. There are two molecules per unit cell. The tetraethylammonium salt is monoclinic with a = 16.3 Å, b = 10.0 Å, c = 12.9 Å, and the angle β = 142°, with two molecules per unit cell. Intensity data was not gathered for these compounds and therefore no bond lengths could be determined.

Bis-tetramethylammonium hexabromouranate (IV) has been reported by Brown[14] to be cubic with the symmetry of the O_h^5-Fm3m space group with a = 13.37 Å. Again, intensities were not found due to difficulty arising from the large absorption problem associated with uranium.

Satten and Young,[8] and references cited therein, have reported the crystal structure of Cs_2UCl_6. This crystal has trigonal D_{3d}^3-C$\bar{3}$m symmetry. Lattice constants are a = 7.614 Å and b = 6.038 Å with one molecule per unit cell. The U--Cl bond distance for this crystal is 2.75 Å.

The crystal structure of $Cs_2UO_2Br_4$ has been reported by Mikhailov, Kuznetsov, and Kovaleva.[15] This has the space group of C_{2h}^5-P2$_1$/c and lattice constants of a = 9.90 Å, b = 9.808 Å, c = 6.39 Å, and β = 103.5°. The uranium has tetragonal bipyrimidal site symmetry. The bromines are located in an equatorial plane with linear UO_2^{++} at an 88°40' angle from this plane. U--Br bond distances are 2.82 Å with a Br--U--Br angle of 94°30'. The U--O bond distance is 1.69 Å. Cesium is located so as to have a coordination number of 10.

EXPERIMENTAL

Preparation of Uranium Tetrachloride

Three grams of uranium trioxide was added to 15 ml of carbon tetrachloride in a thick walled glass ampoule. The ampoule was then sealed, placed in a capped steel pipe for safety, and heated at 125--145°C for 24 hours. The ampoule was opened and placed in a vacuum chamber to remove the carbon tetrachloride. Acetone, saturated with dry HCl, was added to the vessel to dissolve the uranium tetrachloride for use in the preparation of tetraphenylarsonium hexachlorouranate (V).

Uranium tetrachloride was also prepared by allowing 2 grams of uranium trioxide to reflux with 25 ml of hexachloropropene for 24 hours. The product was filtered and washed with ether to remove any organic residue that had formed.

Preparation of Tetraphenylarsonium Hexachlorouranate (V)

One and one-half grams of tetraphenylarsonium chloride was added to 50 ml of ethyl alcohol. To this was added the uranium tetrachloride solution from the above preparation. The resulting solution was allowed to evaporate slowly. The bis-tetraphenylarsonium hexachlorouranate (IV) precipitate that formed was dissolved in a minimum amount of nitromethane. This solution was placed in a vial and dry chlorine gas was bubbled into it. The vial was capped and placed in an oven at 60°C. The solution was rechlorinated after 4 and 12 hours

and left in the oven for another 12 hours after the final chlorination. The precipitate was filtered under dry nitrogen gas and sealed in a vial.

Other attempts to prepare this compound produced only the oxidized bis-tetraphenylarsonium dioxotetrachlorouranate (VI) salt. This occurred when the nitromethane solution was not sufficiently saturated with chlorine.

Preparation of bis-Triphenylphosphonium Hexachlorouranate (IV)

Four and one-half grams of uranyl acetate was added to a 10% solution of HCl in acetone. This solution was then passed over a Jones reductor to reduce the UO_2^{2+} ion to U^{4+}. To a portion of this solution was added enough triphenylphosphine, dissolved in a minimum amount of benzene, to make a 1:1 mole ratio with the U^{4+} in solution. This was allowed to stand for 36 hours at which time a precipitate had formed at the interface of the two solutions. This product was then filtered and washed with cold benzene.

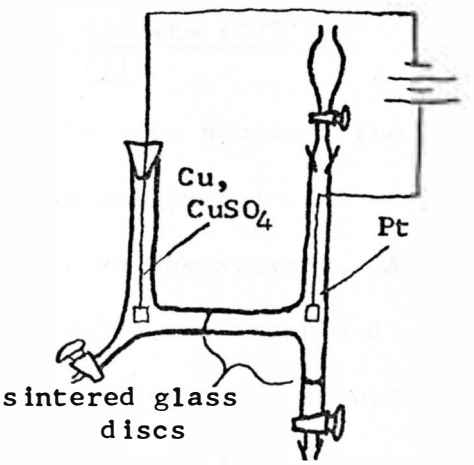
Preparation of bis-Triphenylphosphonium Dioxotetrachlorouranate (VI)

This product was prepared in the same manner as the hexachloro salt, but with the substitution of an ethanol-HCl solution for the acetone solvent.

Electrolysis Reaction

An electrolysis cell was set up using the Cu/Cu^{++} as the oxidation

couple. A platinum electrode was used for the reduction half cell. The uranyl acetate was dissolved in a dilute solution of HCl and KCl in water. The cell, illustrated at right, was then connected to a dc power supply and a current of 25 milliamps was applied to the circuit. After five hours a precipitate had formed on the platinum electrode.



Preparation of bis-Tetramethylammonium Hexachlorouranate (IV)

A U^{4+} solution was prepared in the same manner as the triphenylphosphine salt with acetonitrile used as the solvent. A 10% excess over the stoichiometric requirement of tetramethylammonium chloride was dissolved in 50 ml of concentrated HCl, then added to the U^{4+} solution. This solution was diluted to 400 ml and filtered. The volume of the filtrate was reduced to 20 ml by vacuum distillation. Four hundred milliliters of a 1N HCl solution was added to the flask and the solution was again allowed to distill to 20 ml. This volume was then cooled in an ice bath to crystallize the product which was then filtered and washed with cold acetonitrile. The product was allowed to boil with ethanol to remove any excess of tetramethylammonium chloride.

Anal. Calcd. for $C_8H_{24}N_2UCl_6$: U, 39.74%; Cl, 35.54%.

Found: U, 39.73%; Cl, 35.33%.

Preparation of bis-Tetramethylammonium Hexabromouranate (IV) and bis-Tetramethylammonium Dioxotetrabromouranate (VI)

The procedure used for the uranium (IV) salt also produced the analogous uranium (VI) salt. A U^{4+} solution was obtained in the same manner as for the previous synthesis using water as the solvent. A stoichiometric amount of tetramethylammonium bromide was dissolved in a minimum amount of concentrated HBr and added to the U^{4+} solution. Ethanol was added until the precipitate that had formed just dissolved. 50 ml of acetone was added and the resulting solution was allowed to stand uncovered for four days. Attempts at recrystallizing the uranium (IV) salt consistantly produced the oxidized salt; therefore, the product was used without recrystallization. The uranium (VI) salt was recrystallized from a 50% solution of concentrated HBr and water.

Anal. Calcd. for $C_8H_{24}N_2UBr_6$: U, 27.48%.

Found: U, 27.31%.

Calcd. for $C_8H_{24}N_2UO_2Br_4$: U, 32.25%; Br, 43.36%.

Found: U, 32.33%; Br, 42.95%.

Infrared Spectra

The infrared spectrum was taken for each of the four compounds synthesized in this work: bis-triphenylphosphonium hexachlorouranate (IV), bis-triphenylphosphonium dioxotetrachlorouranate (VI), bis-tetramethylammonium hexabromouranate (IV), and bis-tetramethylammonium dioxotetrachlorouranate (VI). These spectra were all taken on a

Perkin-Elmer 700 infrared spectrophotometer using nujol mulls dispersed on sodium chloride plates.

Visible Spectra

Visible spectra were taken on a Beckman DK2A spectrophotometer. They were all taken between 400 nm and 1500 nm. Samples were prepared as solutions and spectra were run in a 1 cm cell.

X-ray Instrumentation

X-ray diffraction powder patterns were taken on a Picker Nuclear, 6147 series, x-ray diffractometer with the following components: model 809B x-ray generator and control, model 564C high tension transformer, T4OR series four-port copper x-ray tube, model 600084 high voltage power supply, model 644058 pulse height analyzer, model 682047 log-linear ratemeter, model 2811B scintillation detector, Picker 3488 diffractometer, and a Servoriter II portable recorder. A Picker model 681400 powder camera was used for collecting camera powder data. An Enraf Nonius Delft non-integrating Weissenberg camera was used for collecting single crystal data. A Ridl model 49-25 scaler-timer was used in conjunction with the previously mentioned pulse height analyzer to obtain powder intensity data.

Reagents

These chemicals were used as received from the Mallinckrodt Chemical Works:

Uranyl acetate

Ammonium bromide

48% Hydrobromic acid

Sodium peroxide

Benzene

These chemicals were used as received from Eastman Organic Chemical:

Tetraphenylarsonium chloride hydrochloride

Nitromethane

Tetramethylammonium bromide

Tetramethylammonium chloride

Triphenyl phosphine

iso-Amyl acetate

Absolute methanol was used as received from J. T. Baker Chemical Company.

Hexachloropropene was used as received from Aldrich Chemical Company.

Ethanol was used as received from U. S. Industrial Chemicals.

These chemicals were used as received from Matheson Coleman and Bell Chemical Company:

Nitrobenzene

Potassium thiocyanate

1,3-Dibromopropane

Zinc

These chemicals were used as received from Fisher Scientific Company:

Silver nitrate

Tetrabromomethane

Mercury (II) nitrate

Acetone

Density Measurements

Densities were measured by finding the combination of tetrabromomethane and 1,3-dibromopropane in which a crystal would just float when put in a centrifuge. The density measurements (and standardization of pycnometers) were carried out at 22.5°C. Volumes were determined with a 3.7162 ml pycnometer made by R. E. Ashmore at South Dakota State University.

Analysis

Uranium was analyzed by titrimetric oxidation of U(IV) with a standard ceric sulfate solution.[19] Uranium (VI) compounds were reduced in a Jones reductor prior to the titration. Uranium was also determined by igniting the compounds and weighing the residue. This method was checked with uranyl acetate before use. The triphenylphosphonium salts checked in this manner also left a residue of phosphorus pentoxide. By performing both uranium analyses, a phosphorus analysis could also be obtained.

Chloride and bromide determinations were obtained by the Volhard technique, using a sodium peroxide fusion to free the halide ion.

Preparation of Single Crystals

Single crystals of bis-tetramethylammonium dioxotetrabromouranate (IV) were prepared by dissolving the compound in 25% HBr and allowing the liquid to evaporate slowly. A polarizing microscope was used to find a suitable single crystal for x-ray work.

Mounting of a Single Crystal

The crystal was glued to the end of a thin glass rod (approximately 0.3 mm) with Duco Cement diluted with iso-amyl acetate. This glass rod was then mounted on a goniometer head.

Computer Work

The data reduction calculations were performed on the Olivetti-Underwood Programma 101. The IBM 360-40 computer was used for all structure factor determinations, electron density maps, and other related calculations.

Preparation of Samples for Film Method Powder Patterns

Compounds were ground with an agate mortar and pestle so as to pass through a 200 mesh screen, then placed in a 0.5 mm lead free soft glass capillary. This was then sealed with a small flame and held in the camera by a small ball of clay. The sample was aligned by optical means.

Preparation of Samples for Diffractometer Powder Patterns

Crystals were ground to pass through a 300 mesh screen, ground for another half hour, then placed in an aluminum planchet and pressed with a smooth flat iron. Care was taken that the surface of the sample was not pitted. For precision diffraction angle measurements, the compound was mixed with an equal amount of finely divided sodium chloride before pressing it into the planchet.

Method of Obtaining Accurate 2θ Values

The planchet with the sodium chloride mixture was placed in the sample holder of the diffractometer. The diffractometer angle (2θ) was set at 27.33° to correspond to the 100% line of sodium chloride. The sample holder was then adjusted in the x-ray beam to give a maximum intensity reading. An 8° take-off angle was used for all diffractometer work. An aperture slit of .002 cm was used for centering purposes, but was changed to a width of .010 cm for all other work. A nickel foil filter was placed between the sample and the detector to filter out most of the copper $K\beta$ radiation. The gears were placed in the diffractometer to give it a speed of 0.25 degrees per minute. The 2θ value was read off the diffractometer as the peak on the recorder reached its maximum height. A scan of 2θ values from 10° to 75° was recorded. The voltage setting on the x-ray tube was 36 KV with an amperage of 16 ma.

Method of Obtaining Accurate Intensities

Powder intensities were taken on a radiation scaler-timer. A

30-second background count was taken on both sides of the peak where the background was lowest on the ratemeter scan. If the signal between two or more peaks did not return to the baseline, a background count was taken at each end of the region and an average value was used. A diffractometer scan speed of 0.25^{o} per minute was used. The total radiation count over the entire width of the peak was found and the background for the corresponding time was subtracted from the total count. Intensity was taken as being directly proportional to the peak count.

Intensity measurements were obtained for both the pure compound and for the compound mixed with sodium chloride. The sample position was adjusted for maximum peak height for each sample using the 100% line of the uranium salt as the reference. All other diffractometer settings were the same as previously listed.

RESULTS AND CONCLUSIONS

Discussion of Spectra; Visible and Infrared

Visible spectra were used in this study to determine valence states of uranium and relative amounts of U(IV) and U(VI) in various solutions. Infrared spectra were used for qualitative identification and for estimating the U--O bond length.

Uranium (VI) is easily identified by its unique visible spectrum. It has a seven peak cluster occurring at 425 nm $\pm$ 25 nm, depending on the type of ligands and the solvents used. Uranyl acetate has an absorption maximum at 420 nm with very little solvent dependence. Bis-tetramethylammonium dioxotetrabromouranate (VI) has an absorption maximum at 425 nm in dilute HBr. The oxidation product of tetraphenylarsonium hexachlorouranate (V) has an absorption maximum at 450 nm. This distinct area is extremely useful in detecting even small amounts of U(VI).

Because molar absorptivities are not as high, small traces of U(IV) cannot be as easily identified. Major absorption peaks of the product from Jones reductor occurred at 425, 490, 640, and 1075 nm when methanol was used as the uranyl acetate solvent. When acetonitrile was used as the solvent, the peaks shifted to longer wavelengths. A shift of 20--50 nm was observed in all peaks. The U(IV) solution prepared by electrolysis shows a visible spectrum consistant with the latter, while bis-tetraphenylarsonium hexachlorouranate (IV) showed a spectrum which shifted to slightly shorter wavelengths than

the U(IV) in the methanol. A spectrum of bis-tetramethylammonium hexabromouranate (IV) was not obtained since a solvent had not been found that would not oxidize the salt.

Both the visible and the infrared spectra were used to follow the relative amounts of U(IV) and U(VI) salts in the triphenylphosphine reaction. The peak that was followed in the infrared spectrum was due to the U--O asymmetrical stretch and appeared at 895 cm^{-1}.

The infrared spectra of the triphenylphosphine compounds were also used to qualitatively identify the form of the salt produced. The peak at 2485 cm^{-1} is assigned to the P--H stretch and indicates that the salts contain the triphenylphosphonium cation rather than the triphenylphosphine oxide cation.

The U--O stretching vibration in bis-tetramethlyammonium dioxo-tetrabromouranate (VI) was used to approximate the bond distance between uranium and oxygen. This was accomplished in the manner previously referred to and gave a bond length of 1.7 Å.

Discussion of Synthetic Methods

Most preparations of uranium complexes use uranium metal as the starting material. Since uranium metal was not available, a new series of reactions was found to facilitate using uranyl acetate as the starting material.

Uranyl nitrate was heated in air at 450-500°C for one hour and was found to form uranium trioxide which could be used to prepare uranium tetrachloride. However, when the same technique was used

with uranyl acetate, U_3O_8 was formed. As this oxide does not work as well for the preparation of uranium tetrachloride, a different route was needed.

Since a Jones reductor is used to reduce uranium (VI) to uranium (IV) for analytical work, it was believed that this same uranium (IV) solution could be used for synthetic purposes. The first reaction to be tried, the formation of bis-tetraphenylarsonium hexachlorouranate (IV), worked quite well. The visible spectrum of the crude product showed that only a small amount of the U(VI) salt was present. The product was quite pure. When the corresponding U(V) salt was prepared, the visible spectrum again substantiated the fact that very little U(VI) was present.

Tetraphenylarsonium hexachlorouranate (V) is prepared with little difficulty, but it is very unstable to moisture. No analysis of the water oxidation product of the U(V) compound was performed, but it is believed that the product is bis-tetraphenylarsonium dioxotetrachlorouranate (VI). The visible spectrum of the oxidized product shows that only U(VI) is present. The U(VI) salt also appears to be the main product when the nitromethane solution used in preparing the U(V) salt is not sufficiently saturated with chlorine gas.

In the preparation of bis-triphenylphosphonium hexachlorouranate (IV), oxidation of the uranium became a serious problem. This product was never synthesized without a substantial amount of bis-triphenylphosphonium dioxotetrachlorouranate (VI) also being formed. It was found, however, that using acetone instead of methanol as the solvent

in the preparation of the U(IV) solution substantially increased the yield. Relative heights of the U(IV) and U(VI) peaks in the visible spectra were used to investigate this. It is believed that a rigorous control of the water in the U(IV) solution would greatly increase the yield of the U(IV) salt. One way to accomplish this would be to saturate the U(IV) solvent with HCl gas, rather than using concentrated HCl, in order to have the 5-10% HCl solution required for the use of the Jones reductor.

The U(VI) salt could possibly be prepared using water as the solvent. If both of the salts were able to be prepared and purified, a U--Cl bond distance study could be made analogous to the U--Br study presented in this work.

When water was used as the solvent to prepare the U(IV) solution and tetramethylammoniumchloride was added, the product was bis-tetramethylammonium hexachlorouranate (IV). When other solvents were used; acetone, ethanol, etc., a blue product was formed which was apparently a mixture of U(IV) and U(VI) salts, but pure compounds could not be isolated.

In the preparation of bis-tetramethylammonium hexabromouranate (IV), all organic solvents with concentrated HBr added simply gave either the starting salt, tetramethylammonium bromide, or the U(VI) salt as products. This latter product will be discussed below. When water was used, the original salt was again obtained. Ethanol was added to dissolve the precipitate after which acetone was added to precipitate the product. When no precipitate appeared, this solution

was divided into small portions and allowed to stand uncovered in shallow dishes. After two weeks, a precipitate began to appear. In all but one of the precipitating dishes the U(VI) salt, bis-tetramethylammonium dioxotetrabromouranate (VI), was formed. However, one dish contained green crystals which, upon analysis, were shown to be the desired U(IV) salt. Why this one produced a different product has not been determined. A suitable recrystallizing solvent could not be found. Any polar solvent which would dissolve this salt oxidized it to the U(VI) salt. Therefore, the product was used without recrystallization.

The U(VI) salt referred to above, bis-tetramethylammonium dioxotetrabromouranate (VI), was recrystallized from an HBr solution. This would oxidize any of the U(IV) salt present to U(VI). The U(VI) salt could also be prepared analogous to bis-tetramethylammonium hexachlorouranate (IV) using water, ethanol, acetonitrile, or acetone as the solvent.

Since synthetic methods were not the main purpose of this work and ample product had been obtained for further work, no additional research was continued in this area. However, it is believed that the U(IV) salt could be prepared with better consistency by the use of non-aqueous HCl, dissolved in acetonitrile, as the solvent and by using care to keep the system free from moisture.

An electromotive cell was also used in an attempt to reduce U(VI). Solutions of U(IV) were obtained quite readily but any attempt to isolate the solid product, which formed on the electrode, failed.

When the product came into contact with air, it immediately went into solution. Apparently oxidation had occurred. Since U(IV) solutions could be obtained easier with a Jones reductor, further electrolysis work was abandoned.

Discussion of X-ray Techniques

The powder patterns of bis-tetraphenylarsonium hexachlorouranate (IV) and bis-tetramethylammonium hexachlorouranate (IV) are given in Tables I and II respectively. These were obtained by standard Debye-Scherrer camera techniques as stated in an earlier section.

The powder patterns listed in Tables III and IV are of bis-tetramethylammonium hexabromouranate (IV) and bis-tetramethylammonium dioxotetrabromouranate (VI). These powder patterns were obtained by powder diffraction methods. Many unsuccessful attempts were made to find a method of obtaining accurate and reproducible intensity measurements.

Sodium chloride was used to determine the usefulness of the various techniques for sample preparation. To be suitable, the technique was required to produce a sample that would give relative intensities of 100% and 55% to the two most intense peaks of sodium chloride that occur at 27.33° and 45.43° respectively. The first method tried was to grind the sample to an undetermined particle size and place it in an aluminum planchet. The sample was scraped level and held in place with transparent tape. The tape, however, would absorb x-rays at low diffraction angles. Reasonable results were

Table I

X-ray Powder Data for

bis-Tetraphenylarsonium Hexachlorouranate (IV)

2θ	Int_{est}	d_{obs}
8.35	---	10.53
9.20	---	9.600
10.05	70	8.790
11.25	100	7.866
12.20	50	7.245
14.00	90	6.324
15.85	60	5.586
17.80	70	4.980
19.70	50	4.503
20.85	60	4.259
25.20	20	3.535
26.15	20	3.408
27.85	20	3.201
31.13	20	2.872

Table II

X-ray Powder Data for

bis-Tetramethylammonium Hexachlorouranate (IV)

2θ	Int_{est}	d_{obs}	hkl
11.8	100	7.50	111
13.7	50	6.46	200
19.3	80	4.60	220
22.7	70	3.92	311
27.4	45	3.25	400
30.7	45	2.91	331 , 420[a]
33.8	20	2.65	422
35.8	40	2.51	511 , 333[b]
39.3	20	2.29	440
41.0	45	2.20	531
41.7	25	2.17	600 , 442[b]
44.1	15	2.05	620
45.8	15	1.98	533
--	--	--	622
--	--	--	444
50.6	20	1.80	551 , 771[b]
52.6	10	1.74	642
54.0	10	1.70	731 , 553[b]

a Peaks too close to separate.

b Duplicate peaks.

obtained by dispersing a sample passed through a 300 mesh screen with collodian. This method had the drawbacks of not producing a perfectly level surface and oxidizing the U(IV) salt. Petroleum jelly was used to adhere the sample to a glass plate. This method produced usable results, but the sample thickness and uniformity of the surface were poor.

The method finally adopted consisted of grinding the sample until it would pass through a 300 mesh screen and then grinding for one half hour longer. This sample was then pressed firmly into the cavity of an aluminum planchet, using care not to slide the powder while packing. This had a tendency to pack the crystallytes in preferred orientations.

Adding sodium chloride as an internal standard made the preparation of a suitable sample much simpler. This had the effect of eliminating preferred orientations. Intensity values for both uranium salts are averages of pure samples and of samples containing sodium chloride.

A slow scan speed of 0.25° per minute was used for all diffractometer work. Higher scan speeds caused the peaks to appear at a slightly higher 2θ value. Also, when higher speeds were used, 2θ values had to be read off the ratemeter scan. These values would not have been as accurate in that case. The 2θ values in this work are accurate to $\pm 0.02^{\circ}$.

Interpretation of Data

The two uranium bromide complexes in this study were found to be analogous to the corresponding chloride complexes reported earlier. The U(IV) crystal structure is cubic with the uranium being octahedrally surrounded by bromine atoms and having a coordination number of six. The oxidized U(VI) crystal was found to be tetragonal.

Lattice constants and Miller indices were found by applying a least squares refinement to the appropriate equations[16]

$$\frac{1}{d^2} = \frac{1}{a^2}(h^2 + k^2 + l^2)$$

for the cubic system, and

$$\frac{1}{d^2} = \frac{1}{a^2}(h^2 + k^2) + \frac{l^2}{c^2}$$

for the tetragonal system, where a and c are the unit cell dimensions.

Systematic absences of data points were then used to determine space groups into which each of these systems could be placed. It was first believed that space groups reported for the analogous chloride complexes were suitable, those being cubic O_h^5-Fm3m for the U(IV) salt and C_{4h}^5-I4/m for the U(VI) salt. It had also been previously reported that this was the space group for the U(VI) bromide salt.[14] After considerable work had been done in an attempt to refine structures according to these space groups, it was discovered that the systems had been incorrectly assigned. The space groups in question are both centrosymmetric, which means that for every atom at a position of x,y,z within the unit cell, there must be a similar atom at

-x,-y,-z. Uranium, bromine, nitrogen, and oxygen atoms can be put into this arrangement with no trouble. Carbon and hydrogen, on the other hand, must be tetrahedrally arranged about nitrogen and carbon, respectively. Therefore, a non-centrosymmetric space group had to be used.

For the U(IV) system this created no problem. Since the data for the system could be reduced to a 14% residual in the Fm3m space group, it was assumed that the model must be very close to the true structure. Upon careful examination, it was found that the basic difficulty was that this model placed eight carbons centrosymmetrically around each of four of the nitrogen atoms and left the other four nitrogen atoms with no carbon atoms bonded to them. The cubic T_2-F23 space group was found to correct this problem.

The U(VI) system, however, presented a more difficult problem. Since a refinement of less than a 25% residual could not be obtained, it was assumed that there was a basic flaw in our model. Furthermore, there is no non-centrosymmetric body-centered space group and our data clearly indicated body-centering. At this time it was decided to collect single crystal data to check the indexing of the system. This data showed that the crystal was not body-centered, but rather primitive. The reflections corresponding to the criterion that $h + k + l = 2n + 1$ were very weak and therefore were not found in the powder work. The reason these reflections were weak can be explained by the fact that uranium is in a body-centered arrangement and therefore does not contribute. It was necessary then, to find a primitive

space group in which the uranium was body-centered. This space group was eventually found to be either C_4^3-$P4_2$ or C_{4h}^2-$P4_2/m$, the latter being the centrosymmetric equivalent of the first. This determination was made with the help of a Patterson map and will be discussed in a later section.

Intensity data for these crystals was reduced to observed structure factors by the equation

$$F_{hkl,obs} = (I_{hkl}/Lpm)^{\frac{1}{2}}$$

where L and p are the Lorentz and polarization factors. These are correction terms dependent upon the diffraction angle 2θ and for powder work are equal to[17]

$$Lp = (1 + \cos^2 2\theta)/(2\sin^2\theta\cos\theta)$$

The multiplicity of the reflection is referred to by m and is a measure of the number of equivalent Miller indices making up the reflection. These observed structure factors were then compared to calculated structure factors found by the equation

$$F_{hkl} = f_j \sum \cos 2\pi(hx_j + ky_j + lz_j)$$

in a full matrix least squares refinement. The atom positions x, y, and z were varied until a reasonable residual was obtained. The residual is a measure of the error in parameters and is calculated by

$$R = \frac{||F_{obs}| - |F_c||}{|F_{obs}|}$$

The program also refines the structure with regard to temperature parameters. Isotropic parameters were used in the form $e^{-B/4d^2}$ where

B is the temperature parameter and d is the interplaner distance. Since a small number of data points has the effect of raising temperature parameters to unreasonable levels, an upper limit had to be set. Light atoms were not allowed to have a value larger than five and bromine was limited to a value of 3.5

An additional problem was encountered in the solution of the U(IV) cubic salt. Because of the symmetry of the system, more than one set of Miller indices have the same diffraction angle. This differs from multiplicity in that they contain entirely different Miller indices, such as the points 511 and 333. They occur at the same angle because the term of a previously stated equation, $h^2 + k^2 + l^2$, is equal for the indices listed. Fourteen data points were independent. The other ten were related in pairs in this manner.

In order that these points could be used in the calculations, the intensity of the composite had to be divided between the two equivalent points. This was accomplished by calculating intensities from calculated structure factors according to the equation used for finding observed structure factors. The percentage of each intensity, with respect to the sum of the two, was used to divide the observed intensity into the appropriate proportions. This apportionment had to be accomplished periodically throughout the refinement, for as atom parameters were changed, structure factors and intensity percentages changed. A lower R factor could be obtained by leaving out these duplicate points, but the structure can be considered more correct with them included.

Electron density maps were used to find atom positions to be used in the least squares refinement. A fourier summation of the equation

$$P = \frac{1}{V}\sum_h\sum_k\sum_l |F_{obs}|^2 \cos 2\pi(hx + ky + lz)$$

produces a Patterson map which can be used to locate the heavy atoms of uranium and bromine. This map shows electron density peaks corresponding to vectors between atoms in the unit cell. All vectors originate from the origin of the map and therefore the map is extremely difficult to interpret for lighter atoms.

To obtain a fourier map, a fourier summation is applied to

$$\rho = \frac{1}{V}\sum_h\sum_k\sum_l F_{hkl}\cos 2\pi(hx + ky + lz) - \underline{i}\sin 2\pi(hx + ky + lz)$$

where F is the observed structure factor with the sign designated by the calculated structure factor. The heavy atom positions found by the Patterson map are sufficient to fix these signs. The fourier map locates the actual position of the atoms within the unit cell.

The weighting scheme used in the refinement of atom parameters was reported by Baenziger,[16]

$$W = \frac{1}{s_F} = \%s_I F_{hkl} * 0.5$$

where s_F is the standard deviation in F_{hkl}. The quantity used for s_I is[17]

$$s_I = N_T + \underline{k}(N_{BG1} + N_{BG2}) + (0.02N_{PK})^2$$

where s_I is the standard deviation in I_{hkl}, N_T is the total count of

the integrated peak, N_{BG1} and N_{BG2} are the background correction on either side of the peak, and $\underline{k}$ is the peak width. The peak width was determined either by measuring the base of the peak from the rate-meter or by the scan time used to count the peak. N_{PK} is the total peak count minus the appropriate background count.

Structure of bis-Tetramethylammonium Hexabromouranate (IV)

The crystal structures determined here were calculated from powder data rather than single crystal data. This was done in order to take advantage of the accuracy of the x-ray diffractometer available. Also to be considered was the high x-ray absorption due to uranium. With diffractometer powder data, absorption is constant over the entire 2θ range. Absorption is a function of the geometry of the crystal when single crystal data is used. Therefore, absorption corrections necessary in single crystal work are not needed for powder work.

Two problems were involved in using powder data. The first was the indexing of reflections and the other was having reflections with identical diffraction angles. Indexing was accomplished by applying a least squares refinement to the equation

$$\frac{1}{d^2} = \frac{1}{a^2}(h^2 + k^2 + l^2)$$

where a is the lattice constant and d is the interplaner distance. The lattice constant was found to be 13.38 ± 0.01 Å. Other results are listed in Table III.

Table III

X-ray Powder Data for

bis-Tetramethylammonium Hexabromouranate (IV)

2θ	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	hkl
11.46	0.00995	0.00995	111
13.25	0.01329	0.01326	200
18.77	0.02655	0.02652	220
22.02	0.03641	0.03647	311
23.08	0.03995	0.03979	222
26.65	0.05303	0.05305	400
29.89	0.06640	0.06631	420
33.49	0.08287	0.08289	422
34.84	0.08947	0.08952	511 , 333[a]
38.05	0.10609	0.10609	440
39.86	0.11600	0.11604	531
40.42	0.11914	0.11936	600 , 442[a]
42.70	0.13232	0.13262	620
44.58	0.14362	0.14256	533
47.13	0.15956	0.15914	444
48.59	0.16900	0.16909	711 , 551[a]
49.08	0.17221	0.17240	640
52.46	0.19502	0.19561	731 , 553[a]
59.89	0.24875	0.24866	751 , 555[a]

a Superimposed data points.

Table IV

X-ray Powder Data for

bis-Tetramethylammonium Dioxotetrabromouranate (VI)

2θ	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	hkl
12.15	0.01118	0.01112	101
13.39	0.01357	0.01355	110
15.36	0.01784	0.01790	002
19.10	0.02748	0.02710	200
20.45	0.03146	0.03145	112
22.66	0.03855	0.03822	211
24.70	0.04567	0.04592	103
26.92	0.05411	0.05420	220
30.35	0.06841	0.06775	310
33.60	0.08340	0.08313	114
35.52	0.09291	0.09334	231
36.36	0.09718	0.09668	204
39.82	0.11575	0.11550	105
40.52	0.11974	0.11952	411
41.88	0.12748	0.12721	233
43.52	0.13723	0.13733	314
44.38	0.14237	0.14260	215
46.35	0.15462	0.15431	413
49.74	0.17654	0.17648	051
51.92	0.19133	0.19153	334

Table V

Atom Parameters for

bis-Tetramethylammonium Hexabromouranate (IV)

Atom	x/a	y/b	z/c	B
U	0.0	0.0	0.0	0.0
Br	0.1988	0.0	0.0	5.0
N	0.250	0.250	0.250	6.0
C	0.315	0.315	0.315	6.0

Table VI

Atom Parameters for

bis-Tetramethylammonium Dioxotetrabromouranate (VI)

Atom	x/a	y/b	z/c	B
U	0.0	0.0	0.0	0.0
Br(1)	0.223	0.723	0.0	3.0
Br(2)	0.0	0.500	0.253	3.0
Br(3)	0.0	0.50	0.753	3.0
O	0.11	0.61	0.0	4.0
N(1)	0.0	0.0	0.25	4.0
N(2)	0.5	0.5	0.5	4.0
C(1)	0.61	0.50	0.35	4.0
C(2)	0.50	0.61	0.25	4.0
C(3)	0.0	0.11	0.35	4.0
C(4)	0.11	0.0	0.24	4.0

In order to solve the problem of superimposed reflections, the intensities had to be divided between the superimposed points. At the beginning of the refinement, only 14 non-duplicate data points were used. When refinement had been accomplished to an R factor of 0.16, the final 5 data points were apportioned and added to the refinement. This brought the R factor to 0.14 in the wrong space group, as previously mentioned. When it was found that refinement from this point was too slow to be realistic, a new space group was found. This space group, T_2-F23, could not be refined with either the refinement program written by the author or on the least squares refinement program written by Norman Baenziger[20] because of programing difficulties. It was found that the orthorhombic F222 space group is identical to the cubic F23 space group if the three lattice constants are equal. The F222 space group calculations can be used in refinement, providing proper symmetry conditions are imposed.

After the correct space group was found, the R factor dropped immediately to 0.12. Additional refinement of atom parameters gave an R factor of 0.102. This refinement, however, raised the temperature parameters of carbon to unrealistic values. Baenziger[20] states that the B term of the parameter for light atoms should be approximately four. Since only 24 data points were being used (having the effect of raising temperature parameters), a slightly higher value of six was chosen to be the limiting value for carbon. With carbon atom and temperature parameters now held constant, values for bromine parameters were found to vary between 0.1970 and 0.2002 for position

and between 4.5 and 5.3 for temperature. The parameter values were unchanged by the addition of the weighting functions.

The final refinement gave the atom and temperature parameters listed in Table V. These parameters correspond to a U--Br bond distance of 2.66 ± 0.02 Å and a C--N bond distance of 1.47 ± 0.02 Å. The weighting functions used in this work and the structure factors found in the final refinement are presented in Table VII. The R factor for this refinement was 0.0881 based on 19 independent reflections, of which 5 were apportioned to give 24 data points.

Preliminary Work on bis-Tetramethylammonium Dioxotetrabromouranate (VI)

The use of powder data for the structural determination of this U(VI) salt proved to be even more difficult than for the previous example. This crystal was found to be tetragonal with lattice constants of a = 9.35 ± 0.02 Å and b = 11.68 ± 0.02 Å. From the systematic absences in the powder data, this crystal was classified as belonging to the I4/m space group. Body-centered space groups, however, do not allow for the correct placement of carbon atoms tetrahedrally around nitrogen. Also, the Patterson map of these data clearly indicated that there were the same number of bromine atoms in one position along the z axis as there were in two positions, x,$\bar{x}$,o and x,x,o, in the xy plane. This would indicate that there are bromine atoms in the z and $\bar{z}$ directions from both uraniums, but they occupy opposite positions in the xy plane on the two uraniums. This condition definitely rules out a body-centered structure.

Table VII

Calculated and Observed Structure Factors for

bis-Tetramethylammonium Hexabromouranate (IV)

h	k	l	F_{obs}[a]	F_{calc}[b]	W
1	1	1	256	291	1
2	0	0	227	241	1
2	2	0	169	151	2
3	1	1	148	150	4
2	2	2	152	160	2
4	0	0	454	443	4
4	2	0	206	187	2
5	3	1	224	196	2
6	2	0	177	175	6
5	3	3	61	65	99
4	4	4	244	205	99
4	4	0	284	291	7
6	4	0	235	233	4
4	2	2	22	48	99
3	3	3	65	61	2
5	1	1	315	291	2
5	5	1	318	295	5
7	1	1	141	129	5
5	5	3	160	231	13

Table VII (cont.)

h	k	l	F_{obs}	F_{calc}	W
7	3	1	33	48	13
5	5	5	279	288	4
7	5	1	163	158	4
6	0	0	300	370	7
4	4	2	67	108	7

a Scaled.

b $F_{calc}/2$.

It was mentioned earlier that single crystal data were collected at this point to verify the indexing of the powder data. Although the powder indexing was correct, many reflections of weak intensities had not been observed. These reflections did not conform to the systematic absences of the powder work. The single crystal data indicated a primitive space group. The Patterson map showed the uranium atoms to be in a body-centered arrangement. Using these two conditions and the bromine conditions stated above, the space group was found to be either $P4_2$ or $P4_2/m$, depending on the position of the carbon and nitrogen atoms.

If it can be assumed that the nitrogen and carbon atoms will remain in the same positions relative to uranium in the U(VI) complex as in the U(IV) complex studied, the space group would be $P4_2/m$. These positions are shown in Table VI along with other atom parameters found in refinement. The oxygen position was made to correspond to the U--O bond length calculated earlier. Temperature parameters shown were assigned in accordance with values suggested by Baenziger.[20] An R factor of 0.179 was obtained with these parameters. The structure factors and weighting functions are presented in Table VIII.

The computer program furnished by Baenziger was designed for systems of orthorhombic symmetry or lower. Therefore, atom parameters could not be cycled and a fourier map could not be calculated. For these reasons, the structural determination had to be terminated. A manual cycling of bromine atom positions was used to determine the parameters listed in Table VI. The corresponding U--Br bond distance

Table VIII

Calculated and Observed Structure Factors for

bis-Tetramethylammonium Dioxotetrabromouranate (VI)

h	k	l	F_{obs}	F_{calc}	W
1	0	1	271	213	2
1	1	0	257	230	2
0	0	2	215	119	3
2	0	0	238	244	3
1	1	2	183	124	4
2	1	1	164	153	3
0	2	2	138	102	4
0	1	3	156	199	3
2	2	0	335	396	5
0	3	1	94	81	9
1	3	0	203	214	3
0	0	4	408	399	3
2	2	2	150	119	3
1	1	4	242	238	3
2	3	1	172	181	3
0	2	4	159	169	4
0	3	3	125	112	9
4	0	0	212	308	7
0	1	5	148	170	8
4	1	1	138	153	4

Table VIII (cont.)

h	k	l	F_{obs}	F_{calc}	W
3	3	0	177	258	5
2	2	4	293	319	3
2	3	3	156	184	4
2	4	0	99	154	8
1	3	4	151	195	4
3	3	2	110	78	7
1	2	5	133	129	4
4	1	3	107	121	7
1	5	0	334	201	3
0	4	4	290	266	3
3	3	4	164	212	9
2	3	5	119	160	9
4	4	0	105	247	46
3	5	0	51	188	42
2	1	7	196	119	5
6	1	1	38	120	99
4	5	1	149	164	9

of 2.94 ± 0.05 is believed to be accurate to the degree stated despite the high R factor, since varying the position affected the R factor greatly.

Final refinement of this structure will probably find the carbons and nitrogens occupying non-centrosymmetric positions of the $P4_2$ space group. Data from an extremely small single crystal (0.05 mm or smaller per side) may be needed to solve this structure completely. The reflections assumed missing from the powder data could be superimposed on observed values yielding false intensity measurements. The intensity data collected are as accurate as can be obtained on available equipment, even considering this interference. Any further work should be done on a four circle diffractometer so that accurate intensity measurements from a small crystal could be gathered, thus minimizing absorption problems.

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